Borosilicate Glass Formulations for CCIM

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Outline

- Background
- Waste Selection
- Glass Formulation Approaches
- Results of AZ-101 HWL Glass Formulations
- Results of AN-105 LAW Glass Formulations
- Summary of Results
- Path Forward

Background

- Next generation melter (NGM) technologies are being developed to support mission acceleration within the DOE complex
  - Goal is to achieve higher waste throughput rate, which can shorten waste cleanup mission and reduce lifecycle costs

- New glass formulations are being performed to take advantage of NGM technologies
  - This study focuses on cold crucible induction melter (CCIM)
    - Higher melting temperatures
    - Higher waste loading (WL) and increased feed processing rate

- CCIM demonstration tests will be performed to estimate waste loading limits
  - Hanford AZ-101 high-level waste (HLW)
  - Hanford AN-105 low-activity waste (LAW)

Selection of Wastes

- Initially focused on Hanford waste streams
  - Demonstrate highest potential cost benefit to implementation
- Waste compositions were evaluated for their potential to successfully demonstrate the advantages of the CCIM technology over current reference technologies
  - ***AZ-101 HLW: relatively high in Al, Fe, and Zr***
    - Representative approximately 30% of Hanford tank sludge
    - Maximum WL expected for reference WTP formulation methods → 37 wt%
    - Advantages: higher tolerance to crystals and higher melting temperature
      → increase WL and increase processing rate
  - ***AN-105 LAW: low S (WL limited by Na)***
    - Maximum WL expected for reference WTP formulation methods → 27 wt%
      - 21 wt% Na_2O in glass
    - Advantages: higher melting temperature → increase processing rate
      → improve chemical durability of glass
      → increase WL

Waste Compositions

(in wt%)

Oxide	AZ-101	C-104	Bi-Limited	Cr-Limited	Al-Limited	Al&Na-Limited	AN-105	AN-102	AZ-102	AP-101
Al_2O_3	**24.58**	9.69	23.18	27.48	52.95	45.13	17.88	6.4	0.3	5.23
Bi_2O_3	0	0	13.33	7.85	2.53	2.45	0	0	0	0
CaO	1.4	1.67	1.66	2.66	2.38	1.53	0	0.19	0	0
CdO	2.16	0.27	0	0.01	0.05	0.02	0	0	0	0
Cl	0	0	0	0	0	0	**2.17**	1.33	0.07	0.79
Cr_2O_3	0.46	0.4	1.03	3.3	1.15	1.5	0.07	0.09	0.9	0.32
F	0	0	1.63	2.15	1.47	0.48	0.01	0.7	0.56	0.31
Fe_2O_3	**37.67**	17.8	13.83	14.13	13.03	5.95	0	0	0	0
HfO_2	0	14.35	0	0	0	0	0	0	0	0
K_2O	0	0	0.92	0.4	0.31	1.4	1.72	0.66	3.32	19.49
MnO	0.91	3.55	0	0	0	0	0	0	0	0
Na_2O	10.58	11.03	13.39	21.62	7.91	26.88	76.79	84.71	80.57	71.24
Nd_2O_3	0.65	9.97	0	0	0	0	0	0	0	0
NiO	1.66	1.01	3.83	1.14	0.88	0.21	0	0.15	0	0.03
P_2O_5	1.34	1.37	9.91	3.59	2.32	4.27	0	1.15	0.24	0.49
SiO_2	3.77	6.57	12.43	11.36	10.81	6.48	0.1	0.05	0.48	0.1
SO_3	0.38	0.19	0.94	1.64	0.44	0.46	**0.59**	3.89	12.98	1.38
ZrO_2	**11.44**	21.21	0.41	0.12	0.87	0.26	0	0	0	0
Subtotal	97.00	99.08	96.49	97.45	97.10	97.02	99.33	99.32	99.42	99.38
Others	3.00	0.92	3.51	2.55	2.90	2.98	0.67	0.68	0.58	0.62

AZ-101 HLW: relatively high in Al, Fe, and Zr
AN-105 LAW: low S (WL limited by Na)

Glass Formulation Approaches

- Models used to guide glass formulation
  - For HLW
    - Liquidus temperature (T_L) and temperature at 1 vol% spinel ($T_{1\%}$) models were used as qualitative guidelines
    - Product Consistency Test (PCT) and Toxicity Characteristic Leaching Procedure (TCLP) models were used to verify compliance
  - For LAW
    - Existing model was used for PCT
    - New preliminary model was developed for Vapor Hydration Test (VHT) from glasses with high alkali
  - For both HLW and LAW
    - Viscosity and electrical conductivity models were used to predict processing temperature
- Candidate glasses were selected based on key properties

	Crystal Fraction vs. Temperature	CCC Crystallinity	PCT	VHT	TCLP	Electrical Conductivity	Viscosity
HLW	X	X	X		X	X	X
LAW		X	X	X		X	X

Results of AZ-101 HLW Glass Formulations

CCIM-AZ Glasses

(in wt%)

Glass	CCIM-AZ-10	CCIM-AZ-16	CCIM-AZ-17	CCIM-AZ-18	CCIM-AZ-29	CCIM-AZ-30	CCIM-AZ-31	*CCIM-AZ-32*	CCIM-AZ-33
Al_2O_3	11.09	10.44	11.09	11.09	9.79	9.79	9.79	*9.79*	9.79
B_2O_3	**11.00**	**11.00**	**14.00**	**14.00**	**11.00**	**11.00**	**7.00**	***15.00***	**11.00**
CaO	0.63	0.59	0.63	0.63	0.56	0.56	0.56	*0.56*	**4.00**
CdO	0.97	0.92	0.97	0.97	0.86	0.86	0.86	*0.86*	0.86
Cr_2O_3	0.21	0.20	0.21	0.21	0.18	0.18	0.18	*0.18*	0.18
Fe_2O_3	**17.00**	**16.00**	**17.00**	**17.00**	**15.00**	**15.00**	**15.00**	***15.00***	**15.00**
Li_2O	**3.00**	**3.00**	**3.00**	**3.00**	**3.00**	**5.00**	**4.50**	***3.00***	**3.00**
MnO	0.41	0.38	0.41	0.41	0.36	0.36	0.36	*0.36*	0.36
Na_2O	**10.78**	**11.38**	**8.64**	**10.78**	**11.99**	**7.50**	**11.99**	***9.25***	**9.12**
NiO	0.74	0.70	0.74	0.74	0.66	0.66	0.66	*0.66*	0.66
SiO_2	36.59	38.26	35.73	33.59	39.93	42.42	42.43	*38.67*	39.35
ZrO_2	5.16	4.85	5.16	5.16	4.55	4.55	4.55	*4.55*	4.55
Waste Loading, wt%	**45.1**	**42.5**	**45.1**	**45.1**	**39.8**	**39.8**	**39.8**	***39.8***	**39.8**

Predicted viscosity, Pa·s

1250°C	2.6	2.6	2.6	1.8	2.7	2.7	2.7	2.7	2.6
1200°C	4.0	4.0	4.0	2.6	4.0	4.0	4.0	4.0	4.0
1150°C	6.3	6.3	6.3	4.1	6.3	6.2	6.2	6.3	6.3

B_2O_3, Li_2O, Na_2O, and SiO_2 were additive components

Predicted melting temperature: 1200 or 1150°C

Results of Crystal Identification

Identified four crystalline phases containing Fe_2O_3 or ZrO_2 as a major component

Spinel is a primary phase for all glasses

Crystal vol% at each heat treating temperature

T, °C	Crystal	AZ-10	AZ-16	AZ-17	AZ-18	AZ-29	AZ-30	AZ-31	AZ-32	AZ-33
900	Spinel	3.2	2.5	2.6	2.6	2.9	3.5	3.1	2.0	2.0
	Hematite	1.7	1.0	2.8	2.0		0.2		1.6	1.1
	Baddeleyite	0.9	0.5	0.3	0.9					
	Zircon			1.6			0.3		0.3	0.1
1000	Spinel	2.7	2.2	1.7	2.1	1.3	1.8	1.4	1.5	1.5
	Hematite	1.0		2.1	1.1				0.2	
	Baddeleyite	0.8	0.5	0.5	0.9					
	Zircon			1.0			0.3		0.8	
1100	Spinel	1.6	1.3	1.5	1.8	0.9	1.1	0.7	1.0	0.9
	Hematite			1.0						
	Baddeleyite	0.6	0.2	0.8	0.7					
	Zircon									
1200	Spinel	1.5	0.8	1.9	1.5				0.8	
	Hematite			0.3						
	Baddeleyite	0.4		0.5	0.3					
	Zircon									
1250	Spinel	2.3	1.1	1.7	3.2				3.3	
	Hematite			1.0						
	Baddeleyite									
	Zircon									

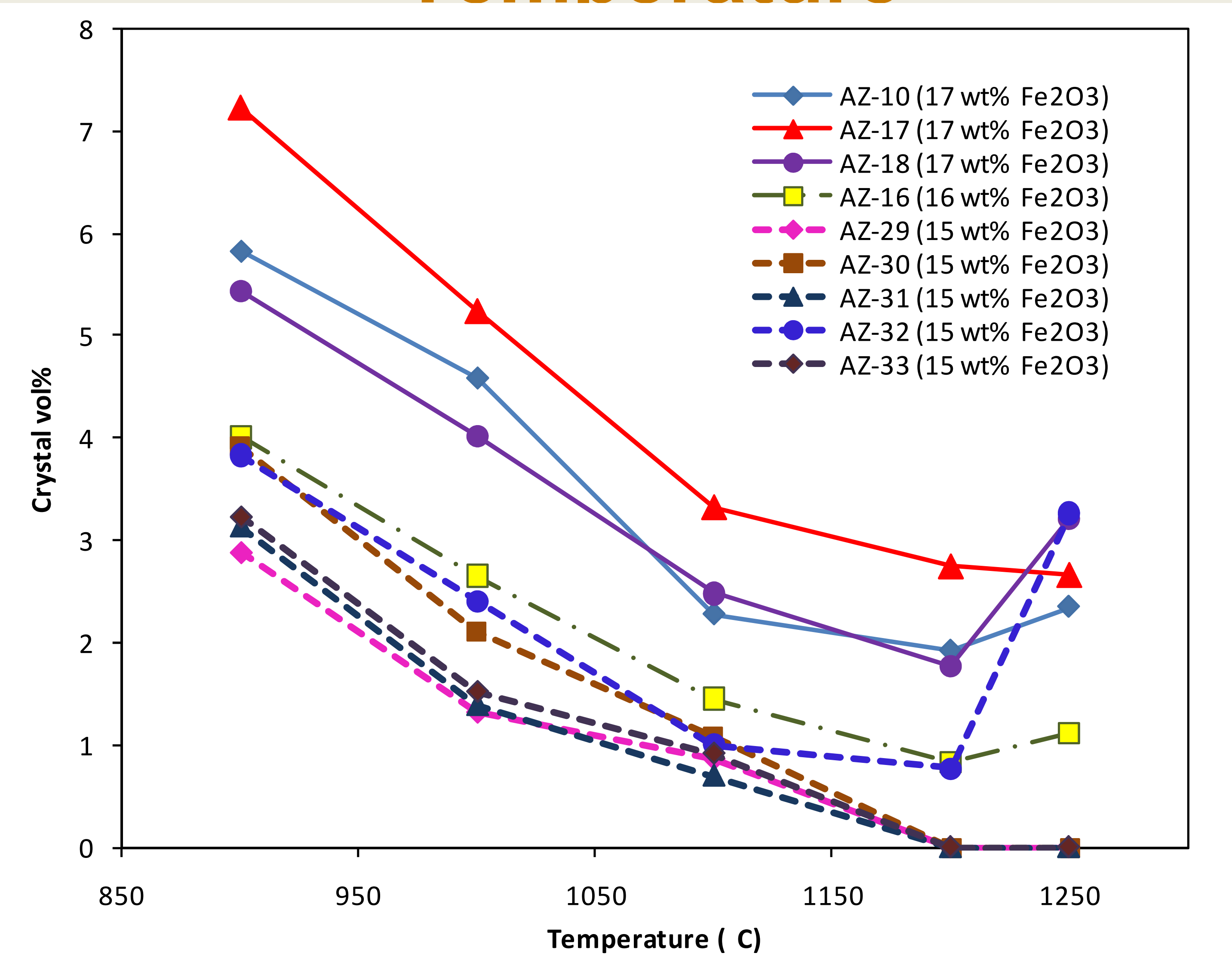
Crystal vol% after CCC treatment

Crystal	AZ-10	AZ-16	AZ-17	AZ-18	AZ-29	AZ-30	AZ-31	AZ-32	AZ-33
Spinel	4.9	4.6	5.0	4.8	5.1	6.1	N/A	4.9	5.0
Baddeleyite	1.0	0.5	1.3	0.8			N/A		

N/A: not analyzed; Empty cell: not detected

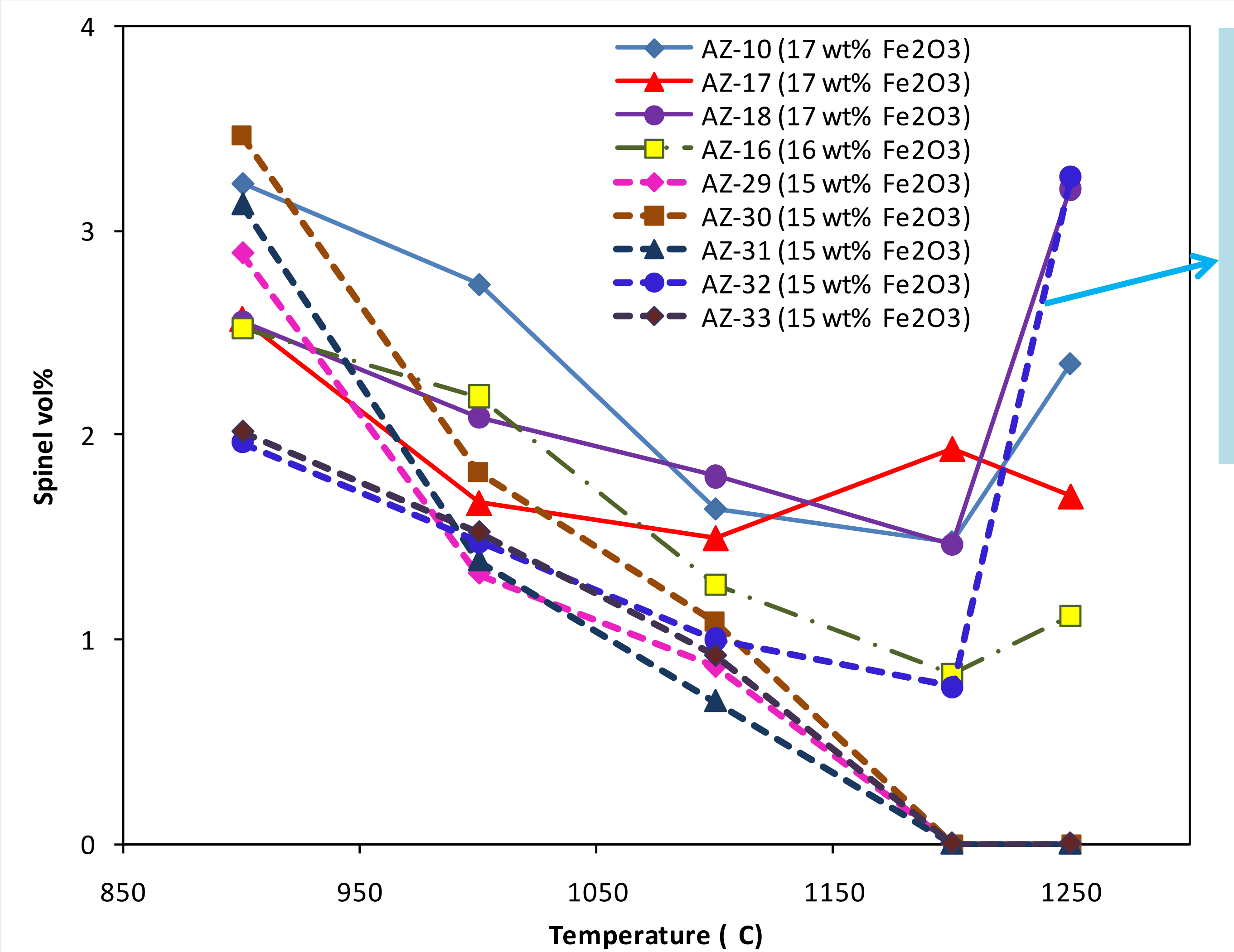
Nepheline ($NaAlSiO_4$) was not formed after CCC

Total Crystal Volume% vs. Temperature



In general, crystal vol% decreases as waste loading decreases and as temperature increases (with exceptions)

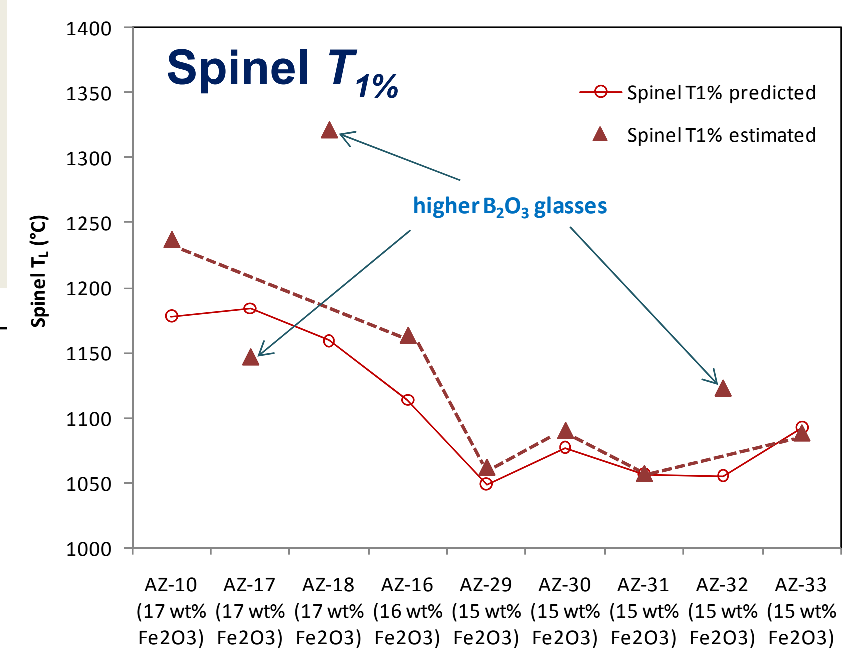
Spinel Volume% vs. Temperature

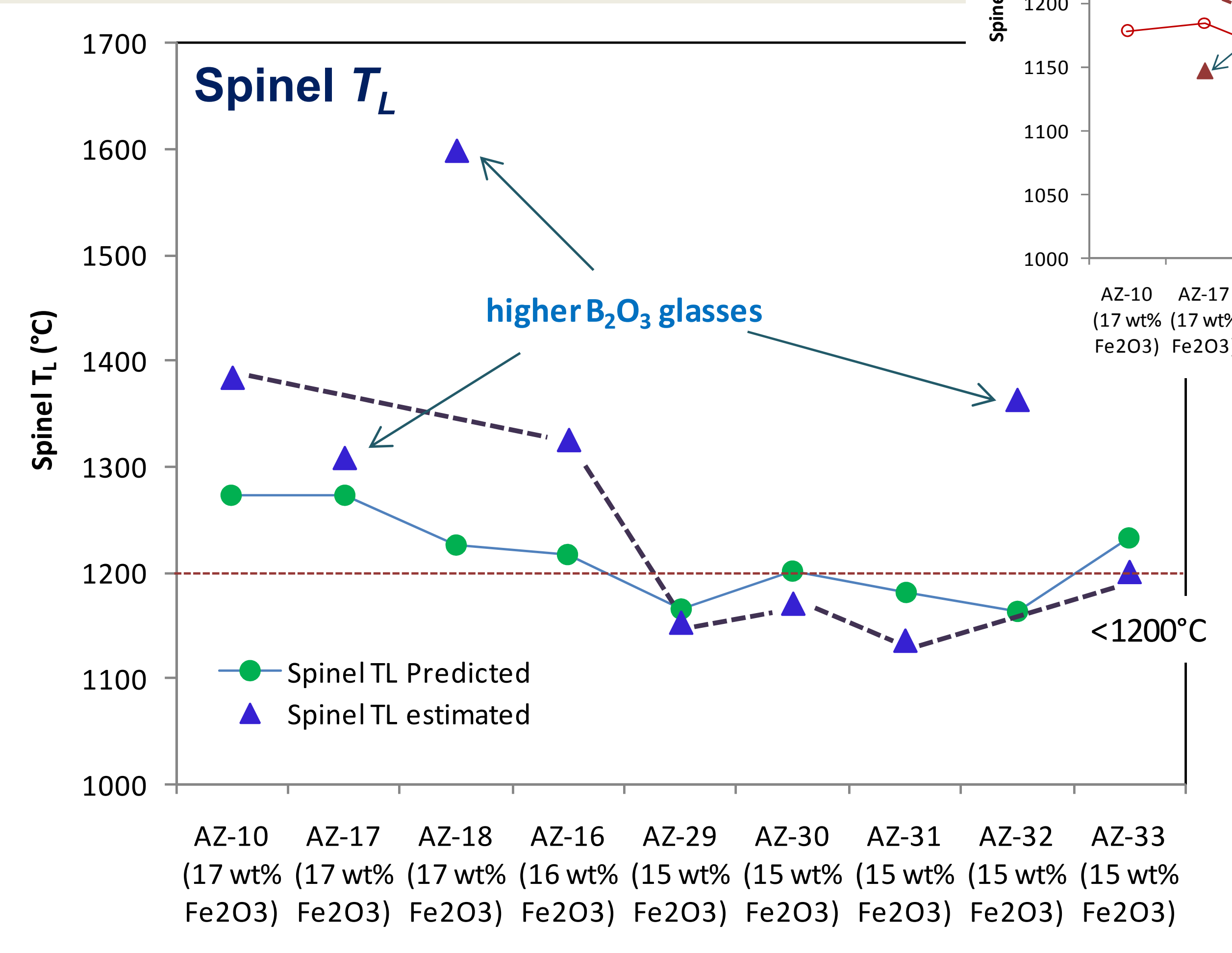


Increase of spinel vol % as temperature increases: caused by extremely small crystals that formed during "quenching" but were not present at heat treating temperature

Liquidus temperature was "estimated" by extrapolating lower temperature data

Estimated Spinel T_L and $T_{1\%}$

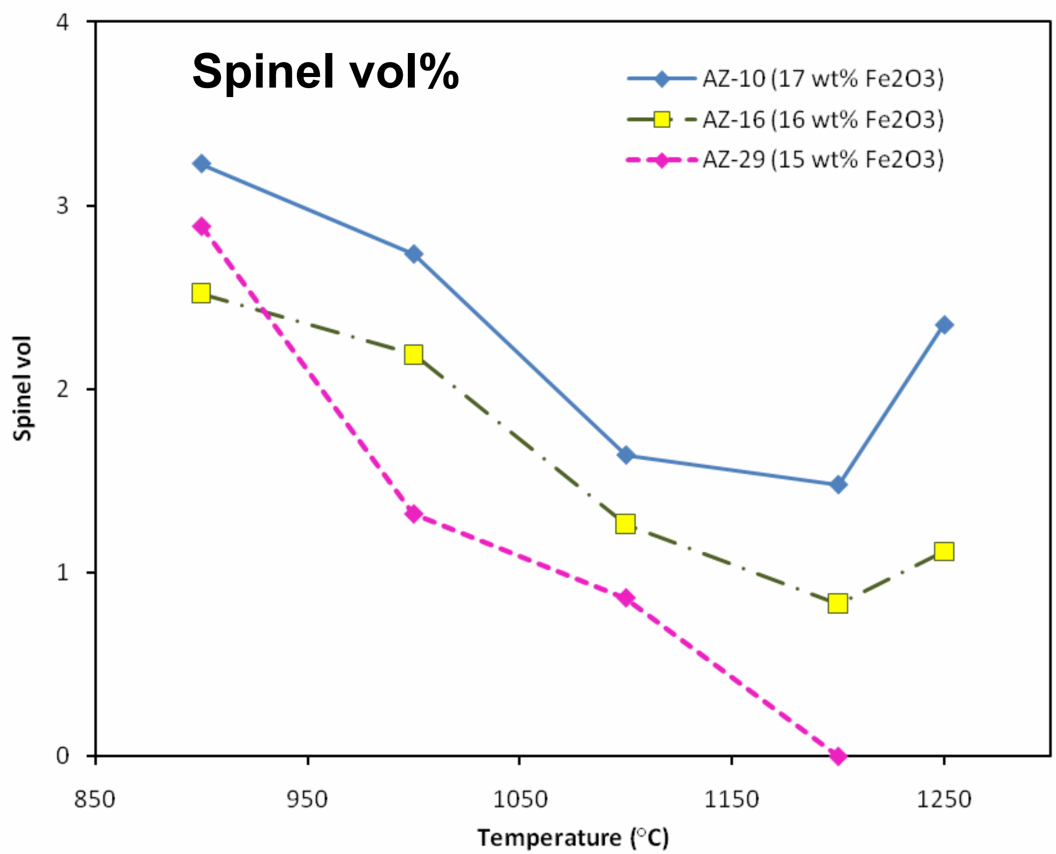


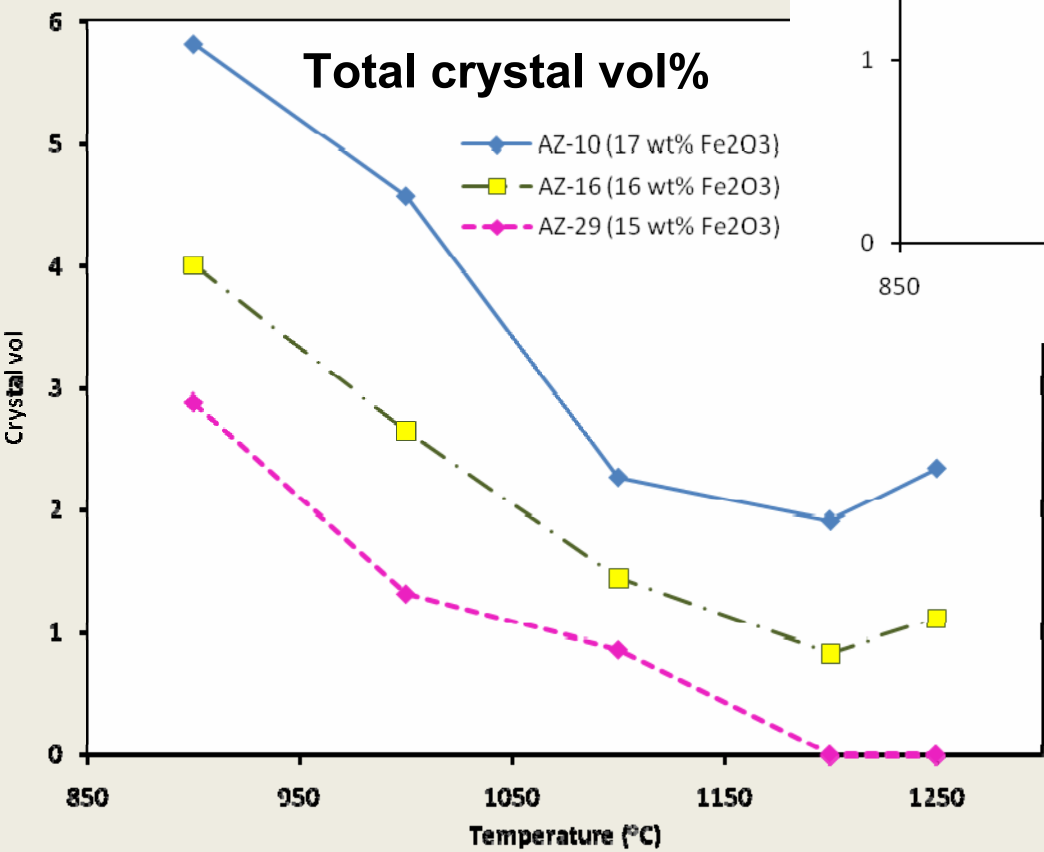


Predicted and estimated values had similar trend for both T_L and $T_{1\%}$ (with exceptions for high B_2O_3 glasses)

Estimated spinel T_L and $T_{1\%}$ are higher than predicted for 16 and 17 wt% Fe_2O_3 glasses, but agree reasonably well with predicted for 15 wt% Fe_2O_3 glasses

Selected Glasses for CCIM





Glass	CCIM-AZ-29	CCIM-AZ-16	CCIM-AZ-10
Al_2O_3	9.79	10.44	11.09
B_2O_3	11.00	11.00	11.00
Fe_2O_3	15.00	16.00	17.00
Li_2O	3.00	3.00	3.00
Na_2O	11.99	11.38	10.78
SiO_2	39.93	38.26	36.59
ZrO_2	4.55	4.85	5.16
Total	95.26	94.94	94.63
WL, wt	39.8	42.5	45.1

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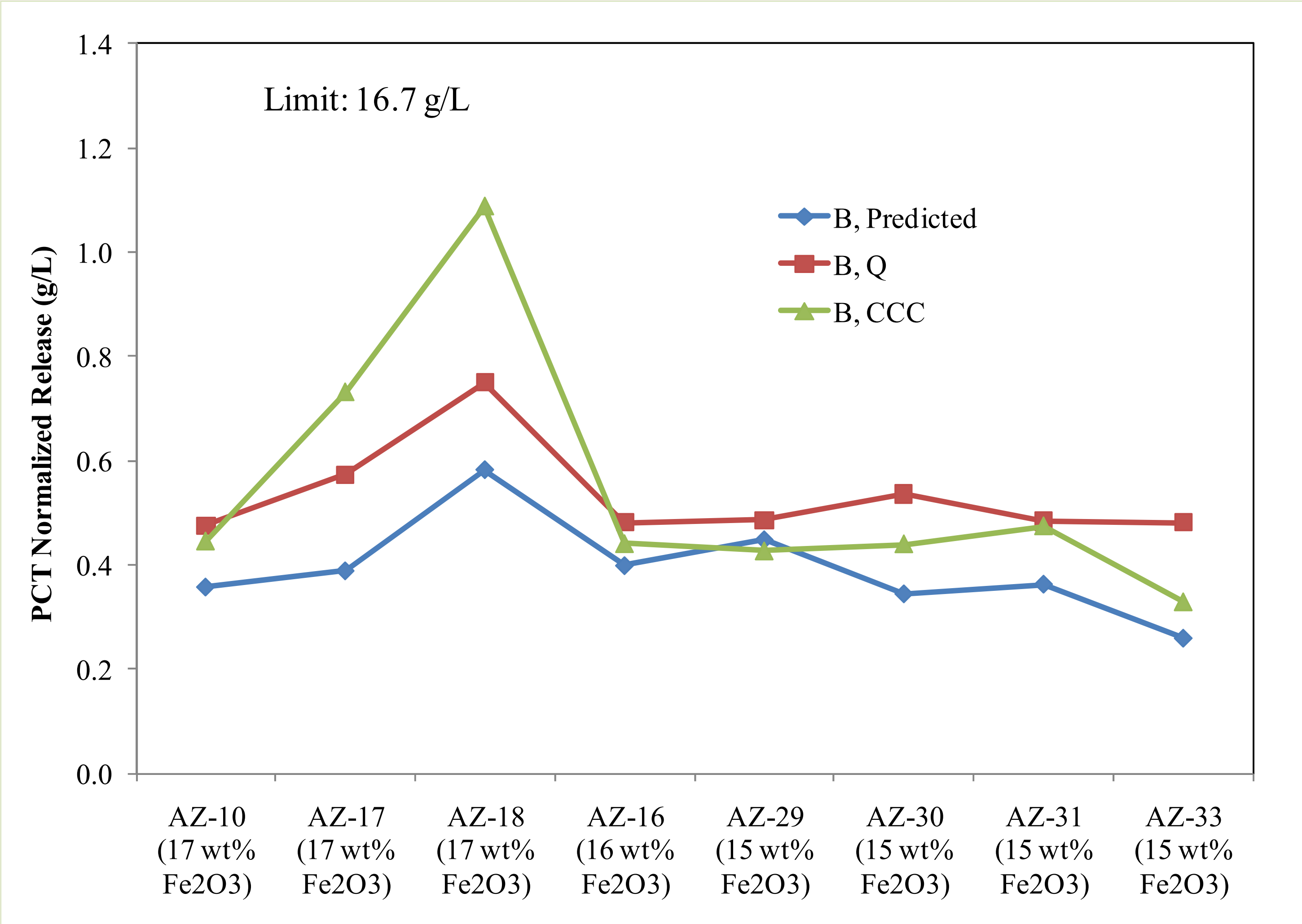
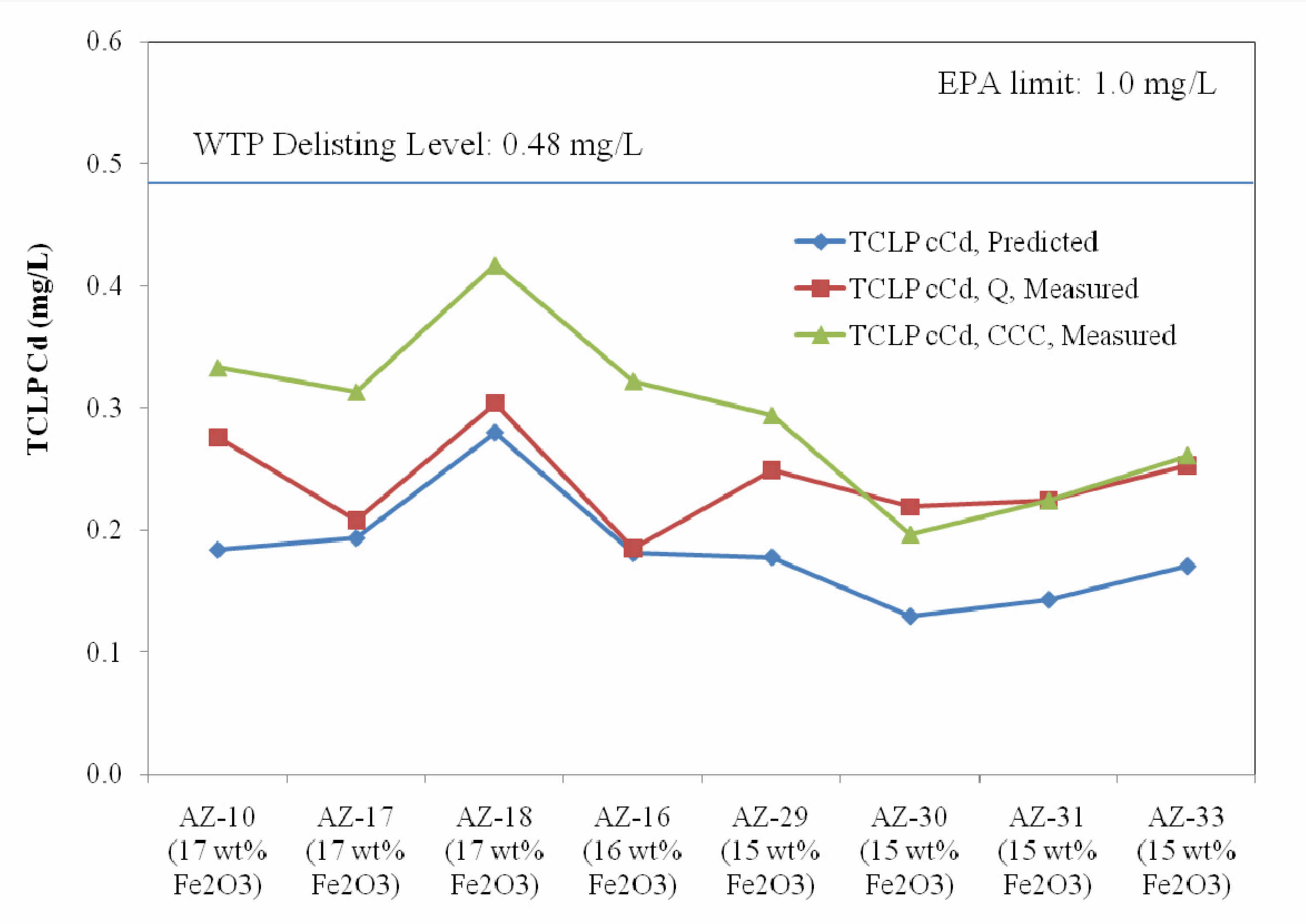
PCT Normalized B Release



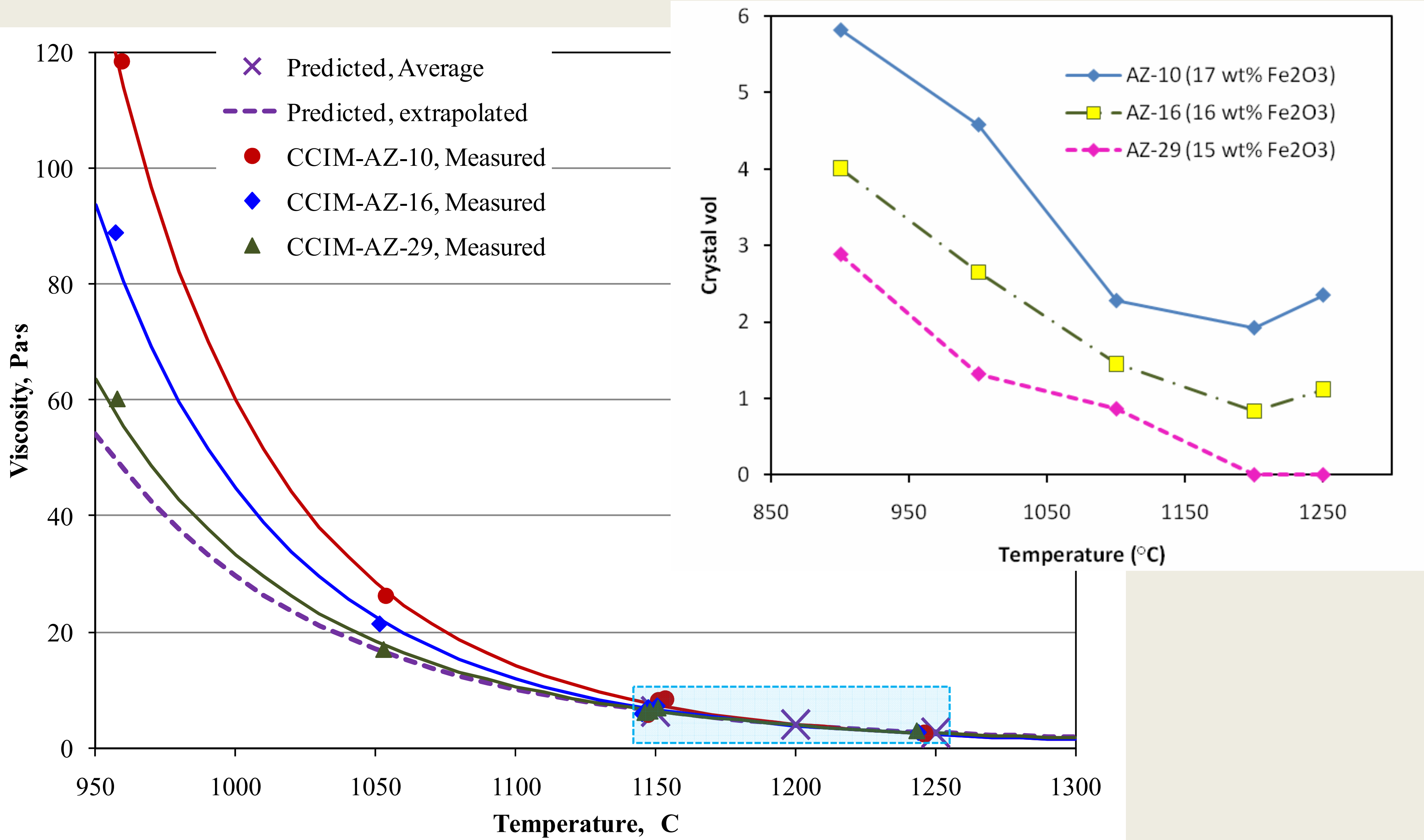
Far below the limit: normalized Na and Li releases had similar results.

TCLP Cd Response



Below the limit for all glasses (AZ-101 is one of the wastes with high Cd concentration)

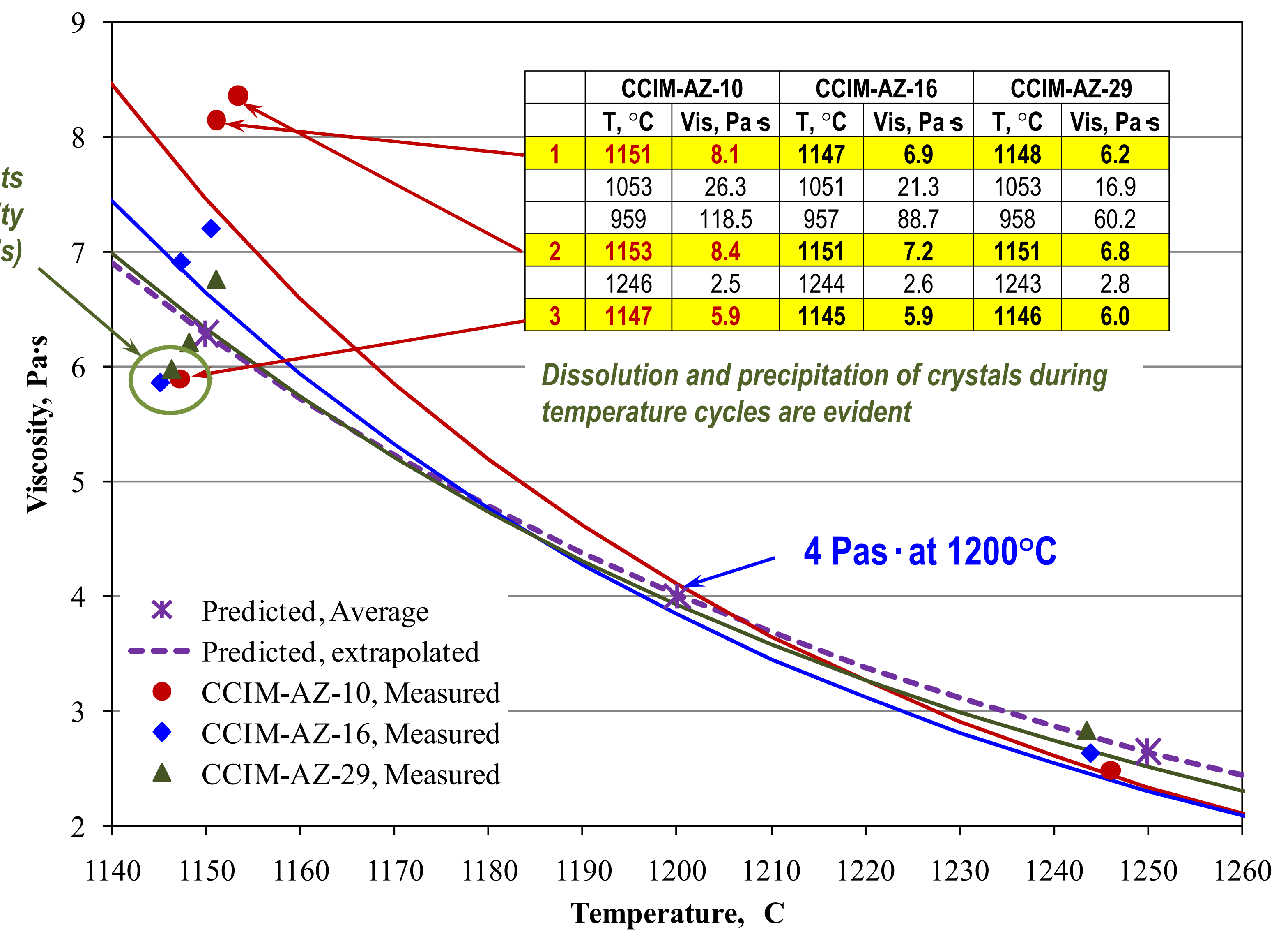
Viscosity of Selected Glasses



All three glasses had similar viscosities that agree reasonably well with predicted values at T ≥ 1150°C
The viscosities at lower temperatures are likely affected by crystal contents

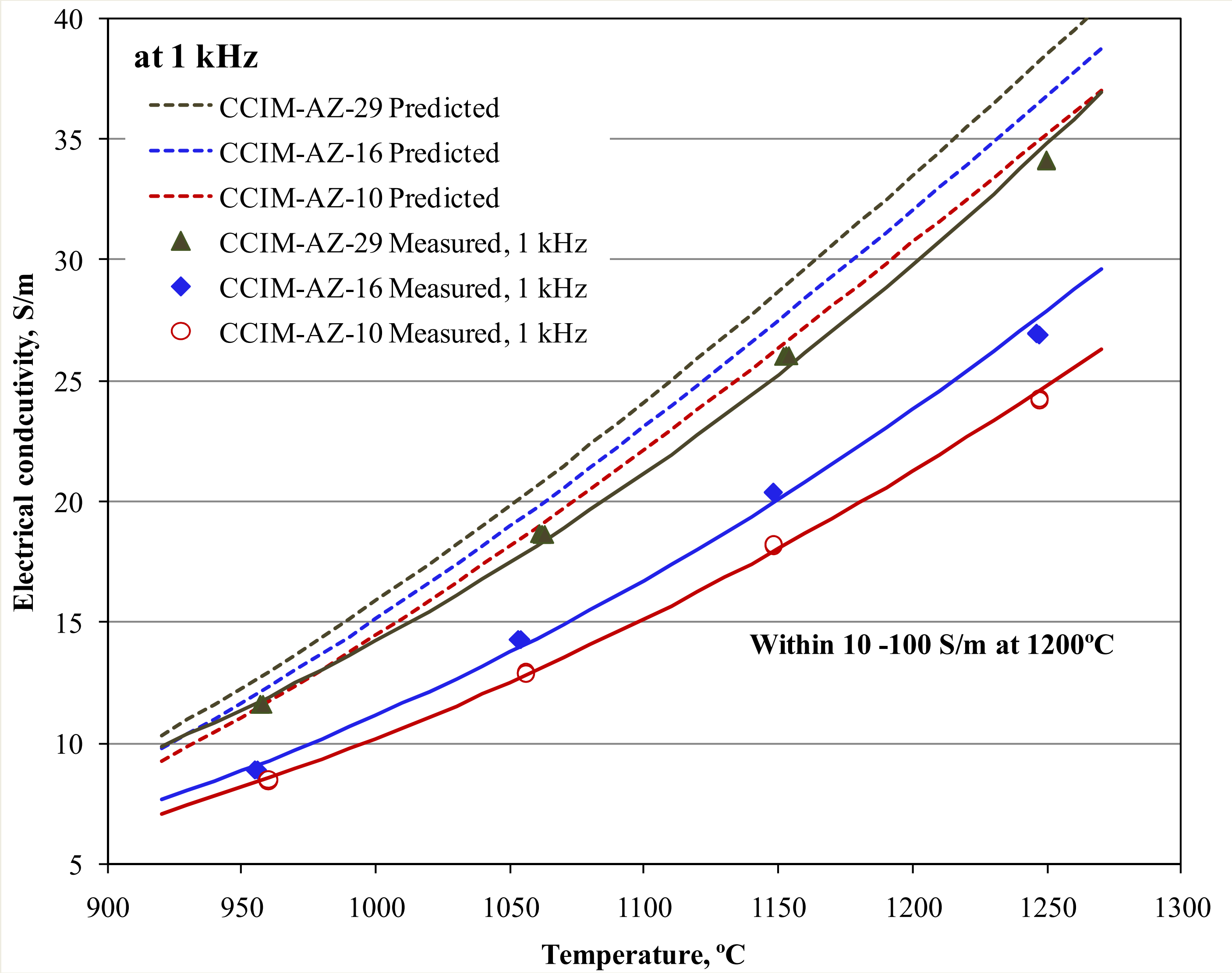
Viscosity of Selected Glasses

Last measurements
All same viscosity
(likely no crystals)



	CCIM-AZ-10		CCIM-AZ-16		CCIM-AZ-29	
	T, °C	Vis, Pa·s	T, °C	Vis, Pa·s	T, °C	Vis, Pa·s
1	1151	8.1	1147	6.9	1148	6.2
	1053	26.3	1051	21.3	1053	16.9
	959	118.5	957	88.7	958	60.2
2	1153	8.4	1151	7.2	1151	6.8
	1246	2.5	1244	2.6	1243	2.8
3	1147	5.9	1145	5.9	1146	6.0

Electrical Conductivity



Measured values are lower than predicted and measured differences between glasses are larger than predicted
But, within the recommended range of 10 to 100 S/m at a recommended processing temperature

Results of AN-105 LAW Glass Formulations

Database for VHT Model Calculation

Group	VSL ORP glasses (24-d)		WTP Model glasses (24-d)		PNNL HLP glasses (varied duration)		PNNL ICV glasses (14-d)		All glasses (converted to 24-d)	
# of glasses	83		86		51		37		257	
	Min	Max	Min	Max	Min	Max	Min	Max	Min	Max
Al_2O_3	**0.058**	**0.136**	**0.050**	**0.090**	**0.040**	**0.120**	**0.080**	**0.168**	**0.040**	**0.168**
B_2O_3	**0.061**	**0.128**	**0.061**	**0.130**	**0.060**	**0.126**	**0.040**	**0.060**	**0.040**	**0.130**
CaO	0.000	0.105	0.000	0.100	0.000	0.050	0.025	0.055	0.000	0.105
Fe_2O_3	**0.000**	**0.030**	**0.000**	**0.100**	**0.000**	**0.158**	**0.040**	**0.110**	**0.000**	**0.158**
K_2O	**0.001**	**0.059**	**0.000**	**0.054**	**0.003**	**0.050**	**0.000**	**0.025**	**0.000**	**0.059**
Li_2O	**0.000**	**0.036**	**0.000**	**0.045**	**0.000**	**0.001**	**0.000**	**0.000**	**0.000**	**0.045**
MgO	0.000	0.034	0.000	0.037	0.000	0.043	0.000	0.030	0.000	0.043
Na_2O	**0.130**	**0.260**	**0.131**	**0.240**	**0.160**	**0.236**	**0.170**	**0.240**	**0.130**	**0.260**
$Na_2O+0.66K_2O+2.07Li_2O$	**0.205**	**0.264**	**0.171**	**0.245**	**0.162**	**0.239**	**0.170**	**0.251**	**0.162**	**0.264**
SiO_2	**0.343**	**0.433**	**0.383**	**0.491**	**0.360**	**0.598**	**0.390**	**0.501**	**0.343**	**0.598**
SnO_2	**0.000**	**0.050**	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.050
SO_3	0.002	0.021	0.001	0.024	0.001	0.003	0.000	0.010	0.000	0.024
TiO_2	0.000	0.016	0.004	0.030	0.000	0.086	0.000	0.020	0.000	0.086
ZnO	**0.010**	**0.037**	**0.010**	**0.050**	0.000	0.043	0.000	0.000	0.000	0.050
ZrO_2	**0.030**	**0.061**	**0.000**	**0.050**	**0.000**	**0.060**	**0.020**	**0.080**	**0.000**	**0.080**
VHT alteration rate, r_{24} (g/m2/d)	2.0	130.0	0.2	108.2	0.4	87.8	0.3	147.1	0.2	147.1
$\ln(r_{24})$	0.693	4.868	-1.609	4.684	-1.004	4.475	-1.146	4.991	-1.609	4.991

Database on glasses with high Na_2O (or high total alkali oxides)
SnO_2: only in VSL ORP data set
ZnO: not present in ICV data set

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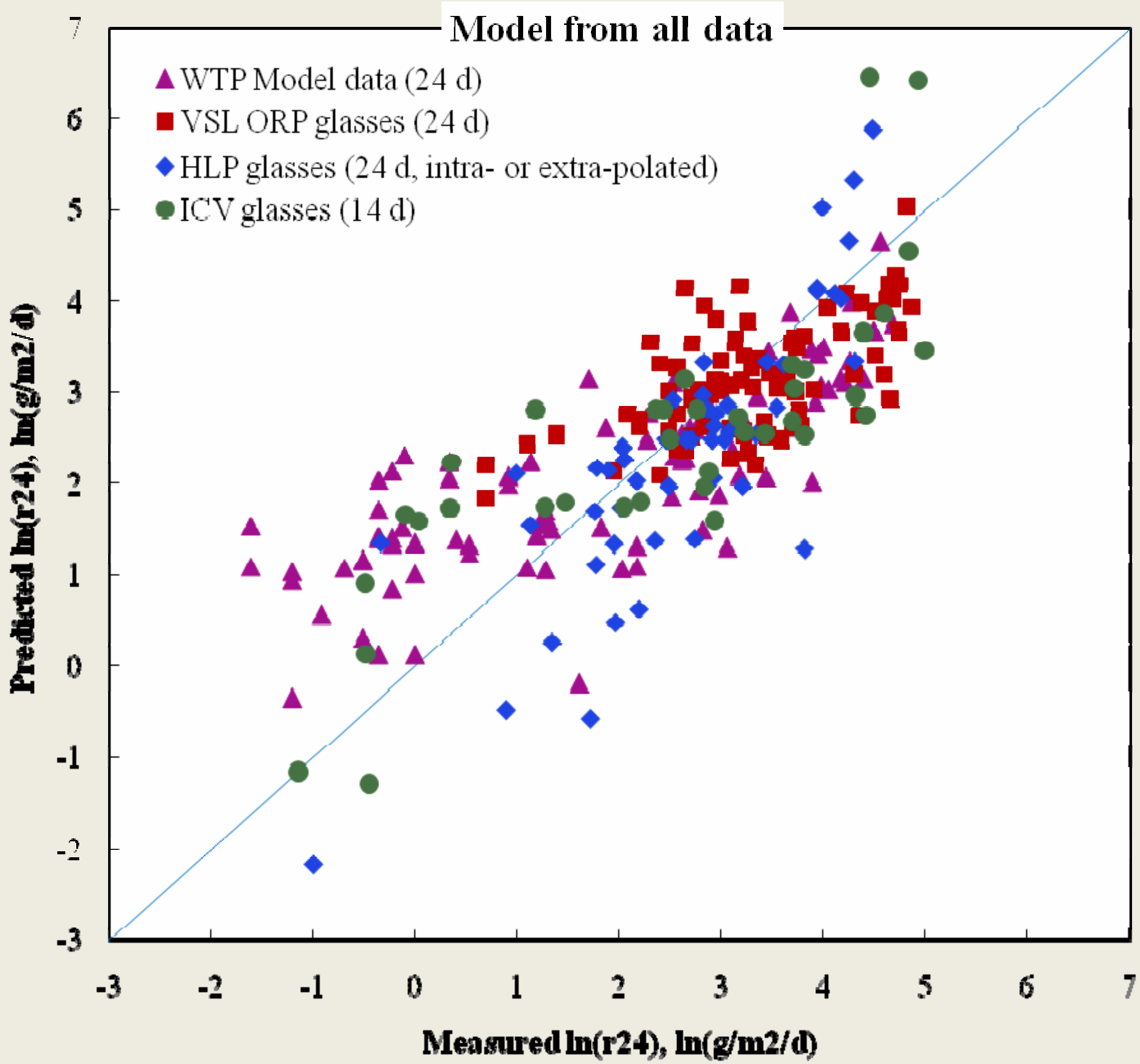
Preliminary VHT Model

# of data	257	
Model	1st order	1st order BC
R^2	0.593	0.593
Al_2O_3	5.2	1.5
B_2O_3	-16.6	-14.7
CaO	-16.4	-16.8
Fe_2O_3	-11.6	-5.5
K_2O	37.8	41.2
Li_2O	117.8	121.6
MgO	-15.7	-19.4
Na_2O	45.4	44.7
SiO_2	-6.5	-6.1
SnO_2	-24.4	-36.1
TiO_2	-8.7	-15.2
ZnO	-28.9	-11.6
ZrO_2	-52.9	-52.3
Others	21.0	17.1

BC: bias correction



Statistical evaluation of data was not performed
→ Model is for general trend only to assist glass development

Glasses Selected for Testing

Oxide (wt)	CCIM-AN-02	CCIM-AN-04	CCIM-AN-09	CCIM-AN-11	CCIM-AN-18	CCIM-AN-20	Limit
Al_2O_3	6.00	6.00	5.59	5.59	6.00	5.82	
B_2O_3	10.37	10.03	9.12	11.58	7.73	8.05	
CaO	0.00	**3.00**	0.00	0.00	**2.00**	0.00	
Cl	0.65	0.65	0.68	0.68	0.68	0.71	
K_2O	0.52	0.52	0.54	0.54	0.54	0.56	
Na_2O	**23.00**	**23.00**	**24.00**	**24.00**	**24.00**	**25.00**	
SiO_2	48.08	45.42	48.68	45.22	47.66	48.45	
SO_3	0.18	0.18	0.18	0.18	0.18	0.19	
SnO_2	2.50	2.50	2.50	2.50	**2.00**	2.50	
ZnO	2.50	2.50	2.50	2.50	**2.00**	2.50	
ZrO_2	6.00	6.00	6.00	**7.00**	**7.00**	6.00	
Total	99.8	99.8	99.8	99.8	99.8	99.8	
Waste Loading, wt%	**29.95**	**29.95**	**31.26**	**31.26**	**31.26**	**32.56**	
T at 4 Pas, C	1250	1200	1250	1200	1250	1250	
EC, S/m	54.33	52.54	59.82	56.85	60.95	66.31	
PCT B, g/L	1.83	1.73	2.00	2.89	1.35	1.93	< 4
PCT Na, g/L	1.78	1.99	2.13	2.56	1.89	2.33	< 4
VHT, $g/m^2/d$	**6.09**	**4.69**	**11.31**	**5.56**	**8.62**	**22.26**	**< 50**
Si/(Si+Al+Na)	0.624	0.610	0.622	0.604	0.614	0.611	>0.62
Optical basicity (OB)	0.582	0.595	0.588	0.587	0.600	0.595	<0.575

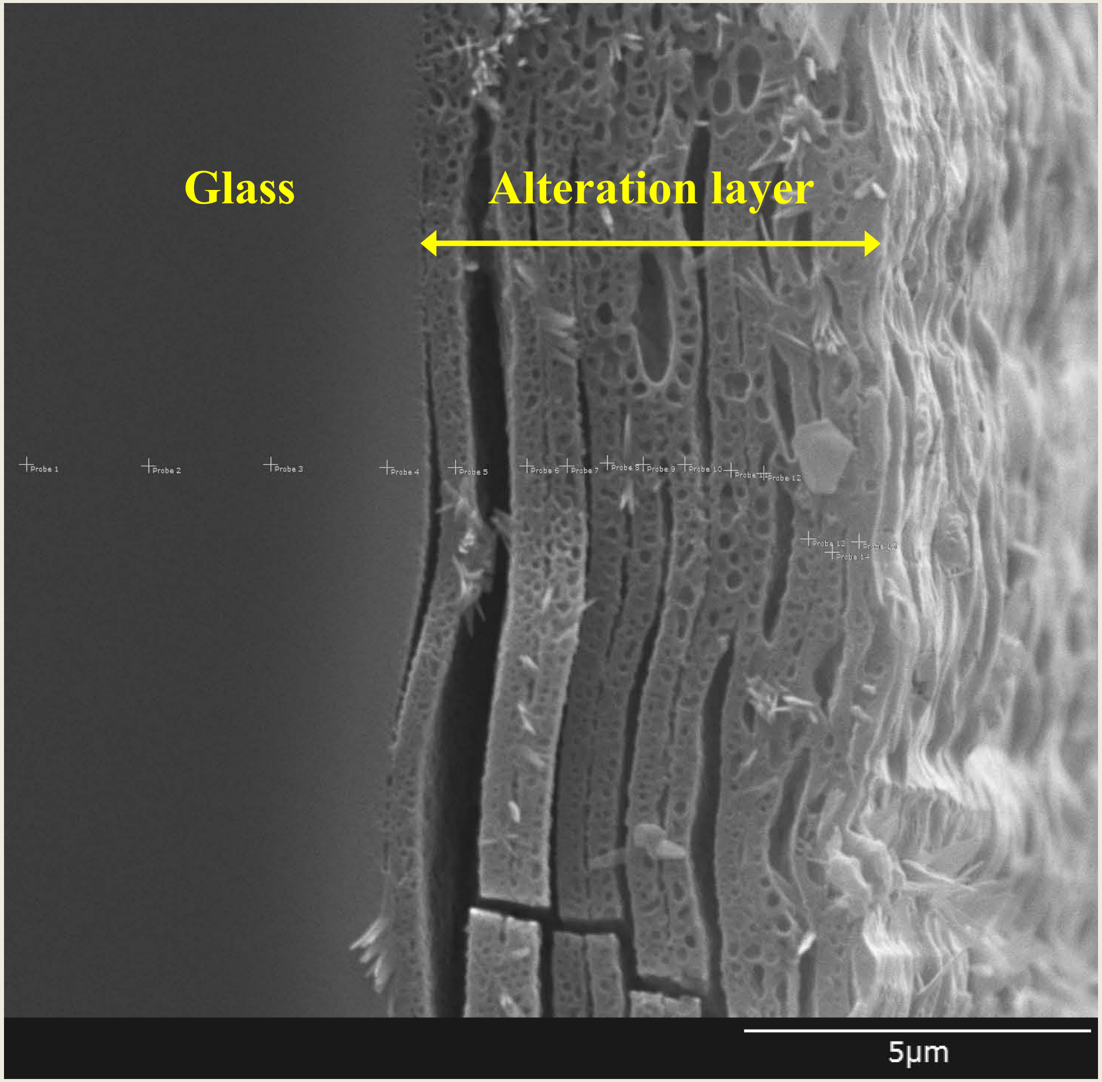
23 to 25 wt% Na_2O (30 to 32.6 wt% WL)
Focused on formulating glasses with low predicted VHT
Predicted melting temperature: 1250 or 1200°C

Si/(Si+Al+Na) and OB are used to predict tendency to nepheline precipitation
(red if outside the desired range, conservative in general)

Summary of Results

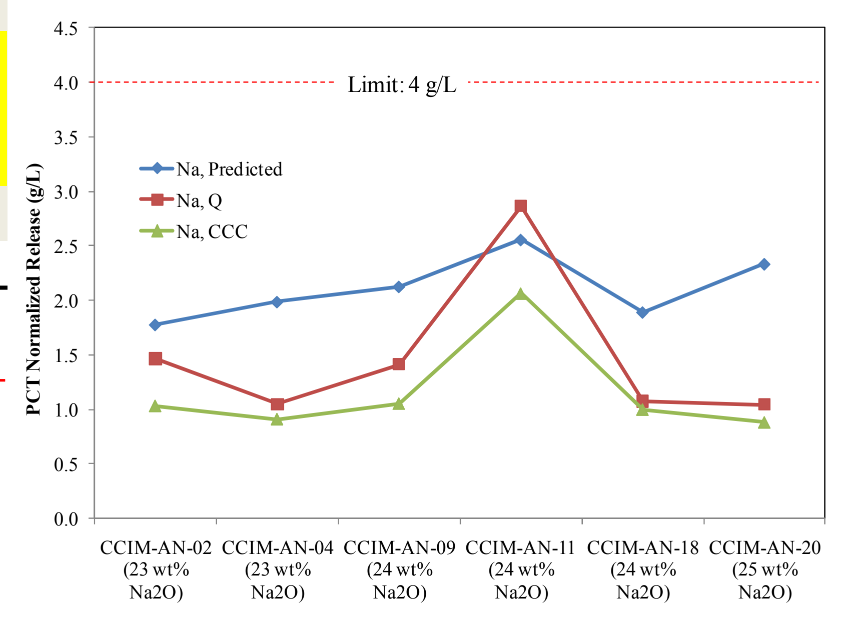
Crystals were NOT detected in all six CCC treated samples
Negligible corrosion by VHT was observed for all quenched and CCC samples

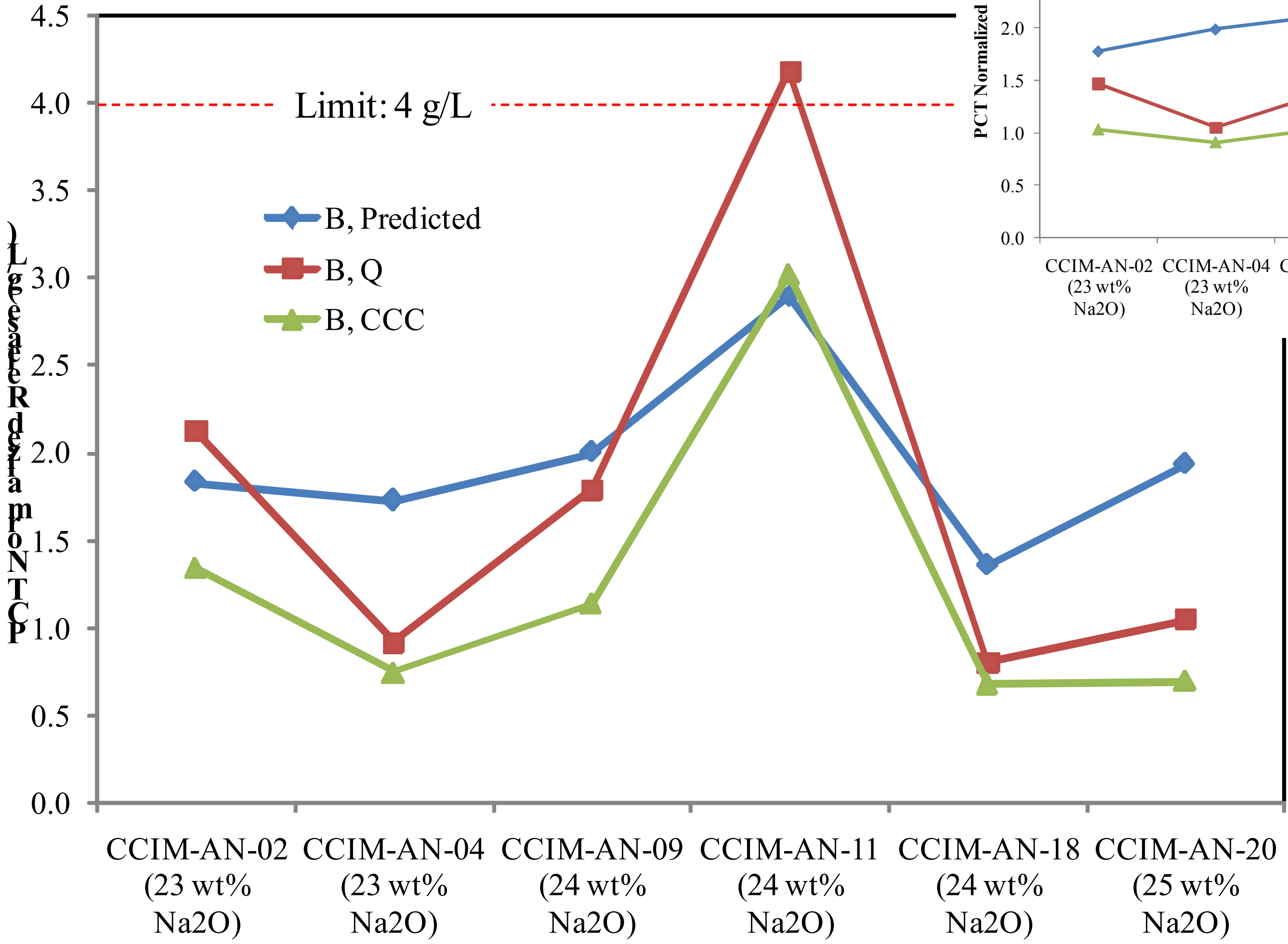
SEM micrograph of VHT alteration layer of CCIM-AN-09 CCC sample after 7-day VHT at 200°C



PCT Normalized Releases

All glasses pass PCT requirements except AZ-11 (PCT B-CCC)
Reasonable agreement between predicted and measured
CCC treatment has no effect or slightly decreases PCT releases



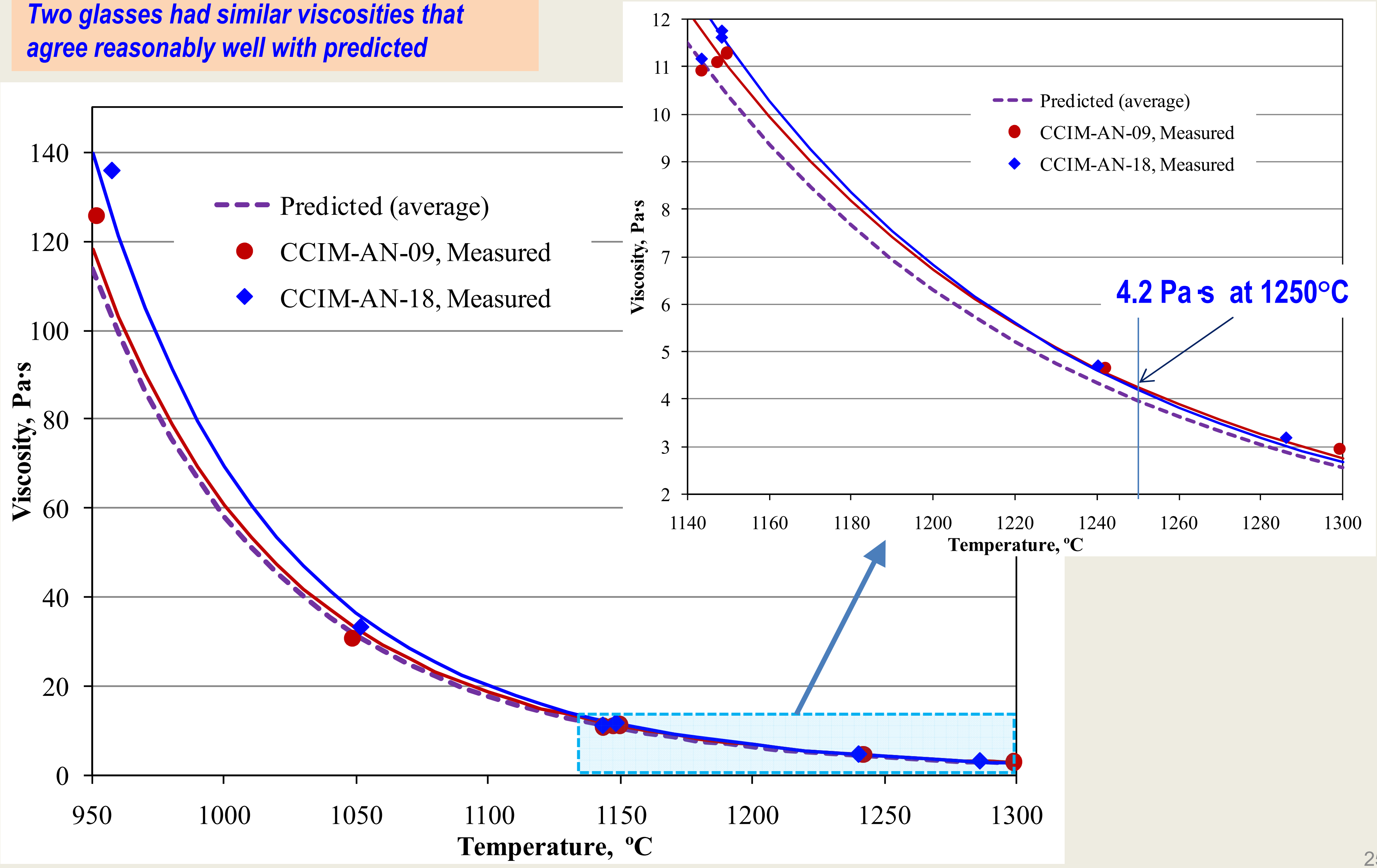


AN-09 and 18 glasses at 24 wt% Na_2O were selected for further testing

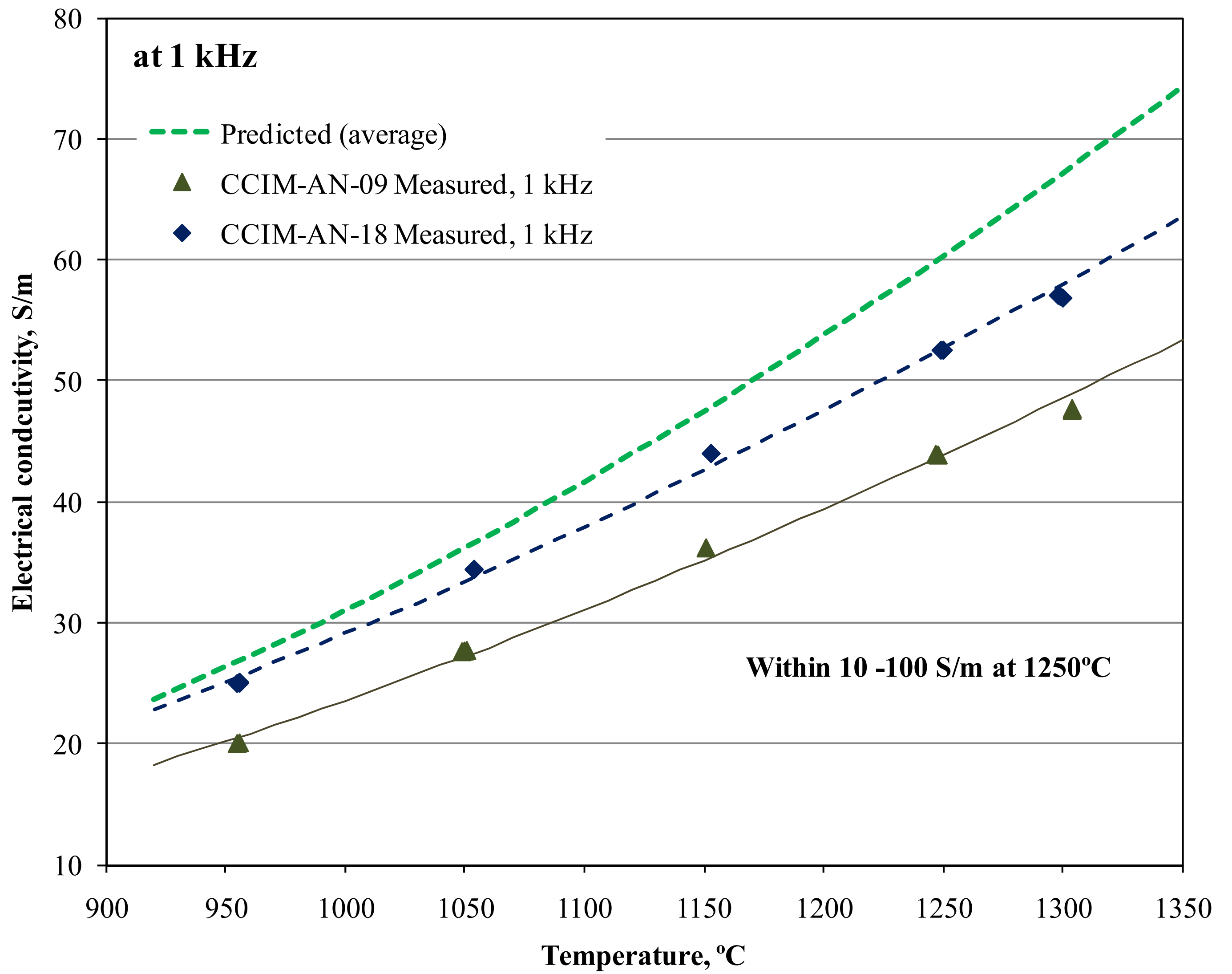
AN-20 glass at 25 wt% Na_2O had analyzed composition significantly off
→ Not selected

Viscosity of Selected Glasses

Two glasses had similar viscosities that agree reasonably well with predicted



Electrical Conductivity



Measured values are lower than predicted,
but within the recommended range of 10 to 100 S/m at a recommended processing temperature

Summary - LAW

- CCIM-AN-18 was selected for the CCIM test
  - 24 wt%Na_2O (31.3 wt% WL)
    - ***14% increase from reference WTP formulation (21 wt% Na_2O)***
  - Recommended nominal processing temperature of 1250°C
    - Measured viscosity of selected three glasses is ~4.2 Pa·s
    - Measured electrical conductivities at 1 kHz is 53 S/m
  - Meet PCT and VHT requirements for both Quenched and CCC samples (no nepheline precipitation)

Summary - HLW

- Three AZ-101 glasses were selected for CCIM tests
  - Fixed concentrations of B_2O_3 and Li_2O

CCIM-AZ-29		CCIM-AZ-16		CCIM-AZ-10
15 wt Fe_2O_3 39.8 wt% WL	→	16 wt Fe_2O_3 42.5 wt% WL	→	17 wt Fe_2O_3 45.1 wt% WL

Crystal content increases as WL increases

22% increase from expected reference WTP formulation (37 wt% WL)

  - Recommended nominal processing temperature of 1200°C
    - Measured viscosity of selected three glasses is ~4 Pa·s
    - Measured electrical conductivities at 1 kHz
      - CCIM-AZ-29 → 30 S/m
      - CCIM-AZ-10 → 24 S/m
      - CCIM-AZ-16 → 21 S/m
  - Meet PCT and TCLP requirements for both Quenched and CCC samples (no nepheline precipitation)

Path Forward

- Glass formulations for LAW
  - Increase loading of AN-105 LAW glass
  - 25 and 26 wt% Na_2O glasses being tested
    - (32.6 and 33.9 wt% waste)
  - Formulation AZ-102 LAW (high S waste) glass
    - Laboratory methods to evaluate salt separation are being developed

- Glass formulations for HLW
  - Select wastes for glass formulations
  - Recent Hanford waste compositions evaluations will be conducted to further select waste streams with greater potential benefits by CCIM technologies